Mild Dehydrogenation of Ammonia Borane Complexed with Aluminum Borohydride

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ABSTRACT: Ammonia borane is a promising hydrogen store. However, its dehydrogenation is stepwise, nonreversible, and accompanied by formation of undesirable byproducts. We report on a new Al(BH4)3·NH3BH4 complex containing 17.7 wt % hydrogen, which undergoes a two-step thermal decomposition below 100 °C. The combination of volumetric, gravimetric, crystallographic, and nuclear magnetic resonance studies shows that both in the solid state and in toluene solutions, the Al-coordinated NH3BH4 already releases two H2 molecules per Al at 70 °C. Contrary to that of the pristine ammonia borane, this process is endothermic, suggesting a possibility for direct rehydrogenation. The dehydrogenation of Al(BH4)3·NH3BH4 contrasts with the complete destruction of alkali and alkaline earth metal borohydride complexes with ammonia borane in the first decomposition step. Other Al-based Lewis acids, less challenging with respect to the stability and safety than Al(BH4)3, may be good agents for supporting the reversible dehydrogenation of NH3BH4 under mild conditions.

INTRODUCTION

In recent years, metal borohydrides M(BH4)n (n = 1, M = Li+ or Na+;2,6,7 n = 2, M = Be2+, Mg2+, or Ca2+;8−10 n = 3, M = Al3+ or Ti3+11,12) have been among the most attractive materials for potential solid-state hydrogen storage as they exceed by far the fuel cells and decreases the reversibility of these potential storage properties consist of metal borohydride complexes with ammonia and ammonia borane, NH3BH4. The presence of N−H°−H°−N−B dihydrogen bonds in these compounds considerably decreases the dehydrogenation temperatures, to the range of 60−250 °C. Several amine metal borohydrides (AMBs) are considered promising hydrogen storage materials: LiBH4·2NH3,22,23 M(BH4)2·2NH3 (M = Mg2+, Ca2+, or Zn2+),24−26 Ti(BH4)3·3NH3,27 Al(BH4)3·nNH3,28,29 Li(Mg(BH4)2)·2NH3,30,31 Li2Ti(BH4)5·5NH3, and Li2Al(BH4)5·6NH3.32 The hydrogen decomposition properties of AMBs are affected both by the nature of the metal cation and by the number of coordinated ammonia molecules per cation. It was reported that LiBH4·NH3 and Ca(BH4)2·2NH3 mainly release ammonia rather than hydrogen under dynamic flow;33,34 however, cobalt-catalyzed thermolysis of LiBH4·NH3 releases 17.8 wt % H2.34 The other representatives, Mg(BH4)2·2NH3 and Al(BH4)3·6NH3, produce only traces of ammonia,24,28 while Zn(BH4)2·2NH3 and Al(BH4)3·4NH3 release high-purity hydrogen under dynamic flow.24,28 The detailed electronic structure of M(BH4)n·2NH3 (M = Mg2+, Ca2+, or Zn2+) reveals a highly ionic character of Ca2+ in Ca(BH4)2·2NH3 and partial covalence of Mg-NH3 and Zn-NH3 which prevents the release of NH3 from the latter complexes.35

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Despite the high hydrogen content of ammonia borane (\(-19.6\%)\) and acceptable stability upon transportation and storage, \(\text{NH}_3\text{BH}_3\) undergoes stepwise decomposition with 6.5% hydrogen released below 112 °C and 14.5% near 200 °C, all accompanied by undesirable borazine and aminoborane \(\text{NH}_2\text{BH}_3\). A considerable improvement is achieved by transforming aluminum anion \(\text{Li}_2(\text{NH}_2\text{BH}_3)(\text{BH}_4)/\text{LiNH}_2\text{BH}_3\), were obtained in recent years.\(^{42,43}\) All the listed MABs release hydrogen as well as toxic ammonia and traces of \(\text{NH}_3\text{BH}_3\). For the mixed MAB–AB complex \(\text{LiNH}_2\text{BH}_3:\text{NH}_3\text{BH}_3\), the hydrogen release was reported to occur at 14.0 wt % in a stepwise manner at 80 and 140 °C, and neither borazine nor aminoborane was detected.\(^{44}\) Metal borohydride–ammonia borane complexes \(\text{M(BH}_4)_n(\text{NH}_2\text{BH}_3)_m\) \((n = 1, m = 1 \text{ or } 2 \text{ for } \text{M} = \text{Li}^+; n = m = 2 \text{ for } \text{M} = \text{Ca}^{2+} \text{ or } \text{Mg}^{2+})\) showed more facile hydrogen release below 112 °C and 140 °C, and neither borazine nor aminoborane was detected.\(^{45}\) The decomposition temperature to \(-90^\circ\text{C}\) for \(\text{Li}_2\text{Al(BH}_4)_5(\text{NH}_3\text{BH}_3)_3\) was measured independently using a PILATUS 2M pixel detector (Oxford Cryosystems). For better completeness, two crystals were measured at \(100^\circ\text{K}\) under a nitrogen flux. \(\text{Al(BH}_4)_3\) and \(\text{NH}_3\text{BH}_3\) were selected in \(\text{NH}_3\text{BH}_3\) were aged at room temperature for 2 months. The residues were dissolved in \(\text{toluene-d}_8\) and measured at \(295^\circ\text{K}\) under a nitrogen flux.\(^{55}\) The Rietveld method was used for the phase analysis and refinement with Fullprof Suite.\(^{55}\)

\[ \text{AlCl}_3 + 3\text{LiBH}_4 \rightarrow \text{Al(BH}_3)_2 + 3\text{LiCl} \] (1)

We used the same procedure described in our previous work,\(^{16}\) which is a modification of an earlier one.\(^{51}\) The final product is obtained by the following addition reaction:

\[ \text{Al(BH}_3)_2 + \text{NH}_3\text{BH}_3 \rightarrow \text{Al(BH}_3)_3\text{NH}_3\text{BH}_3 \] (2)

For that purpose, 1 mL of freshly obtained liquid \(\text{Al(BH}_3)_2\) is injected via syringe into a bottle with 70 mg of \(\text{NH}_3\text{BH}_3\) powder. The bottle is kept sealed for 72 h until large white crystals form (Figure S1 of the Supporting Information). The excess of liquid \(\text{Al(BH}_3)_2\) was pumped off during 30 s. The obtained crystals self-ignite when they come into contact with moisture and air.

\[ \text{X-ray Single-Crystal Analysis.}\] The complex reveals two polymorphs. The crystals of \(\text{Al(BH}_3)_3\text{NH}_3\text{BH}_3\) were selected in the argon-filled glovebox and then measured at 100 K under a nitrogen flux (Oxford Cryosystems). For better completeness, two crystals were measured independently using a PILATUS 2M pixel detector and \(\lambda = 0.82103 \text{Å}\) synchrotron X-ray radiation at the SNBL beamline, ESRF (Grenoble, France). The recorded data were indexed in monoclinic space group \(P2_1/c\) with \(a = 7.8585(2)\ \AA,\ b = 6.8647(1)\ \AA,\ c = 15.7136(8)\ \AA,\ \beta = 96.429(4)^\circ\) and integrated by CrysAlisPro.\(^{52}\) The collected absorption correction was applied. The data from the two crystals were integrated separately and scaled (not merged) in XPREP (Bruker) prior to structure solution and refinement.

\[ \text{Data for } \beta\text{-Al(BH}_3)_3\text{NH}_3\text{BH}_3 \text{ were collected on a MAR345 image plate detector (Mo Kα radiation, Zr filter). The crystals of } \beta\text{-Al(BH}_3)_3\text{NH}_3\text{BH}_3 \text{ were loaded into inert grease in an argon-filled glovebox and then measured at 295 K under a nitrogen flux (Oxford Cryosystems). The recorded data were indexed in a monoclinic cell and integrated with CrysAlisPro, and the absorption correction was applied.}\] The structure was determined in space group \(C\) with \(a = 10.8196(8)\ \AA,\ b = 7.2809(4)\ \AA,\ c = 11.3260(9)\ \AA,\ \beta = 107.69(1)^\circ\) with a pseudo-inversion symmetry for 83% of the structure, as determined by ADDSYM in Platon.

All single-crystal structures were solved by direct methods and refined by a full matrix least-squares method on \(F^2\) using SHELXL2014.\(^{53}\)

\[ \text{X-ray Powder Diffraction.}\] For variable-temperature \(\text{in situ}\) X-ray diffraction, the crystals of \(\alpha\)- and \(\beta\)-Al(BH\(_3\)_3)\(_{\text{NH}}\text{BH}_3\) were ground in an agate mortar inside the argon-filled glovebox and the powders were introduced into 0.7 mm glass capillaries that were sealed with vacuum grease. The capillaries were heated from 20 to 100 °C with a nitrogen flow (Oxford Cryosystems) with heating rates of 1 and 0.2 °C/min. The two-dimensional data images obtained at SNBL were azimuthally integrated with Fit2D using LabX as a calibrant.\(^{54}\)

\[ \text{NMR Spectroscopy.}\] NMR spectra were acquired in toluene-\(d_8\) on a Bruker Avance DRX500 spectrometer operating at 500.1 for \(^1\text{H}\) (160.5 MHz for \(\text{^11B}\) and 130.3 MHz for \(\text{^27Al}\)). Chemical shifts are reported with reference to \(\text{SiMe}_2\text{ (TMS)}\) for \(\text{^1H}\), \(\text{BF}_3\text{OEt}_2\) for \(\text{^11B}\), and 1.1 M \(\text{Al(NO}_3)_3\) in \(\text{D}_2\text{O}\) for \(\text{^27Al}\). Spectra were measured on solutions of \(\alpha\text{-Al(BH}_3)_3\text{NH}_3\text{BH}_3\) crystals, as well as on the starting products \(\text{Al(BH}_3)_3\) and \(\text{NH}_3\text{BH}_3\) dissolved in toluene-\(d_8\) for reference. After dissolving the crystals of \(\alpha\text{-Al(BH}_3)_3\text{NH}_3\text{BH}_3\), we measured the evolution of spectra with time, fresh after 2 h, and after 18 h. Other samples studied by NMR were aged at room temperature for 2 months and heated under argon up to 70 °C and up to 100–110 °C in sealed glass bottles using a mineral oil bath for 40 and 60 min, respectively. The residues were dissolved in toluene-\(d_8\) and measured at room temperature.

The deconvolution processing for \(\text{^27Al}\) NMR spectra included one level of zero filling, exponential multiplication of the free induction decay with a line broadening (lb) factor of 1 Hz, Fourier transform, and zero-order phase correction; no correction of the initial decay, no first-order phase correction, and no baseline correction were applied. The region between 8700 Hz (66.76 ppm) and 7700 Hz (59.09 ppm) was submitted to deconvolution analyses using a homemade program developed in Excel. The \(\text{^27Al}\) NMR signal was described as a first-order multiplet, constraining intensity ratios according to Pascal’s triangle and imposing a Lorentzian shape and identical line width for all of the components. A second-order polynomial (three adjustable parameters) accounted for the local baseline.

\[ \text{NMR data of the compounds recognized in the presented spectra.}\] \(\text{^27Al}\) NMR δ 17.6–17.8 (s, \(\text{^1J}_{\text{AB}} = 132\text{ Hz},\) external hydrogen), \(\text{^27Al}\) NMR δ 44 Hz, bridging hydrogens), \(\text{^11B}\) NMR δ 17.6–17.8 (s, \(\text{^1J}_{\text{AB}} = 132\text{ Hz},\) \(\text{^11B}\) NMR δ 21.8 (quadruplet, \(\text{^1J}_{\text{AB}} = 92\text{ Hz},\) \(\text{^13C}\) = 33.8 (quint, \(\text{^1J}_{\text{AB}} = 88\text{ Hz},\) \(\text{^11B}\) NMR δ 21.9 (s, \(\text{^1J}_{\text{AB}} = 34.1\text{ s,}\) \(\text{^11B}\) NMR δ 60.3 (s, broad); \(\text{^27Al}\) NMR δ 60.3 (s, broad).

Decomposition product, presumably \(\text{Al(BH}_3)_3\text{NH}_3\text{BH}_3\) or its oligomer:
Using a Hiden Analytical HPR-20 QMS sampling system. The samples one NH3BH3 molecule, forming a mononuclear Al(BH4)3 powder. NH3BH3 at room temperature gives white crystals (see Mettler and DSC 821 Mettler devices with heating rates of 1 and 5 °C/min for both) in an argon flow of 20 mL/min. The decomposition up to 200 °C was measured by a ThermoStar GSD 301T spectrometer coupled with a simultaneous TGA/DTA 851 analyzer. Four decomposition experiments were conducted under a nitrogen flow of 10 mL/min to prevent hydrolysis or oxidation.

Mass spectrometry (MS) analysis of the residual gas was performed using a Hiden Analytical HPR-20 QMS sampling system. The samples (each approximately 2 mg) were loaded into an Al2O3 crucible and heated from room temperature to 70 °C, fixing this temperature for 2 h (1 °C/min for both) in an argon flow of 20 mL/min. The decomposition up to 200 °C was measured by a ThermoStar GSD 301T spectrometer coupled with a simultaneous TGA/DTA 851 Mettler device. The released gases were analyzed for hydrogen, ammonia, diborane, and borazine in both experiments.

Volumetric Study. Volumetric analysis was performed using a Hiden Isochema IMI-SHP analyzer. Four decomposition experiments with the Al(BH4)3-NH3BH3 complex were conducted with 50–60 mg of sample, under a 5 bar back-pressure of hydrogen/helium, from 30 to 70 °C and from 30 to 100 °C at a heating rate of 1 °C/min. The gas release was calculated from the calibrated volumes of the system, excluding the volume of the glass wool (2.06 g/cm³). Rehydrogenation of the samples decomposed at 70 and 100 °C was conducted at ~150 bar of hydrogen, by heating them to 70 and 100 °C and cooling them to 30 °C at a rate of 0.1 °C/min.

RESULTS AND DISCUSSION

Al(BH4)3-NH3BH3 can be obtained from commercially available chemicals, AlCl3, LiBH4, and NH3BH3, in two steps. The synthesis requires an inert atmosphere as the intermediate Al(BH4)3 is highly pyrophoric. The reaction of Al(BH4)3 with powder NH3BH3 at room temperature gives white crystals (see Figure S1 of the Supporting Information). The reaction was allowed to proceed on average for 3 days. Ball milling is expected to dramatically accelerate the reaction on a large scale; however, one should avoid extended vacuum pumping of the excess Al(BH4)3, as it decreases the yield of the product.

The detailed characterization of the complex is presented below. It aimed first to identify its different crystal forms coexisting under ambient conditions, second to improve our understanding of its complex dehydrogenation, and third to determine the nature of the Al-based intermediate species.

Crystal Structure of the Complex. We have characterized two polymorphs of Al(BH4)3-NH3BH3: the low-temperature α-phase and the high-temperature β-phase. α-Al(BH4)3-NH3BH3 is observed only in freshly synthesized samples, while it slowly transforms at room temperature into the β-phase. In both structures, aluminum atoms coordinate three BH4− anions and one NH3BH3 molecule, forming a mononuclear Al(BH4)3·NH3BH3 heteroleptic complex, like the one shown in Figure 1. Weak dihydrogen bonds between BH4− and -NH3 groups associate the complexes into a three-dimensional structure. N−H−...H−H−-B bonds are often bifurcated on the N−H side; thus, the H−H distances are rather long, exceeding 2.6 Å, while N−H−...H−H− angles are not very close to 180° (see Table S6 of the Supporting Information).

The Al3+ cation is linked via BH4− edges to three BH4− anions and to one ammonia borane molecule. With respect to B atoms, Al adopts a distorted tetrahedral coordination, and the AlH8 polyhedron has the shape of a snub disphenoid, like that of Mg in Mg(BH4)2 structures. This contrasts with planar AlB2/trigonal prismatic AlH4 coordination in both known polymorphs of Al(BH4)3. It is nearly identical to the 2.22–2.26 Å Al−B distances in K[Al(BH4)4] and [Ph3PMe3][Al(BH4)4], where the Al3+ cation is also coordinated to eight hydrogen atoms. The interatomic Al−B distances involving ammonia borane’s BH4− group are slightly longer (2.31 Å) than the distances to the BH4− anions. They are still much shorter than metal−boron distances in other borohydride−NH3BH4 complexes, namely, 2.63–2.92 Å in (LiBH4)2-NH3BH4, LiBH4-NH3BH3, and Ca(BH4)2: 2NH3BH3. The Al−H bond distances vary accordingly: they range from 1.65(8)–1.81(1) Å where BH4− is involved, similar to those in Al-based complex hydrides, to 1.86(1)–1.96(8) Å where the BH4− group is involved. The latter are much shorter than the 2.44 and 2.50 Å Al−H bond distances in Ca(BH4)2: (NH3BH4)3 and the 2.08–2.32 Å distances in (LiBH4)2: NH3BH3.

Relative Stability of the Polymorphs. The phase analysis by X-ray powder diffraction was performed prior to further characterization of the complex by other techniques. Both α- and β-Al(BH4)3-NH3BH3 can be obtained as single phases using the synthesis procedures described above (Figure 2). Figure S2 of the Supporting Information shows Rietveld refinement profiles for single-phase samples of the α- and β-polymorphs. α-Al(BH4)3-NH3BH3 was found as a single phase only in freshly prepared samples. Within a few days at room temperature, we find a mixture of the two phases. The crystals of the β-phase cooled to 100 K did not turn into the α-phase; thus, the α to β transition is irreversible or at least slow.

Variable-temperature in situ powder X-ray diffraction of both polymorphs at a heating rate of 1 °C/min (Figure 3) reveals that α-Al(BH4)3-NH3BH3 undergoes a first-order phase transition to β-Al(BH4)3-NH3BH3 at ~26 °C; the latter is melting and presumably decomposing at ~71 °C. The heating of the single-phase sample of the β-phase with a 5-fold lower
rate of 0.2 °C/min reveals melting at the lower temperature of 52 °C (see Figure S3 of the Supporting Information), thus confirming the simultaneous decomposition.

**Raman Spectroscopy.** The Raman spectrum of β-\(\text{Al(BH}_4\text{)}_2\cdot\text{NH}_3\text{BH}_3\) is shown in Figure 4. Several stretching B–H modes can be recognized in the 2080–2600 cm\(^{-1}\) range, similar to the vibrational modes of \([\text{Al(BH}_4\text{)}_4]^-\) and \(\text{Al(BH}_4\text{)}_3\text{NH}^-\), where \(\text{BH}_4^-\) is coordinated to \(\text{Al}^{3+}\) in a bidentate manner.\(^{22,61}\) Three intense peaks at 2441, 2496, and 2530 cm\(^{-1}\) probably belong to the outward B–H (terminal) stretching modes from different BH\(_4\) and BH\(_3\) groups; the peaks from 2040 to 2300 cm\(^{-1}\) correspond to inward B–H (bridging with Al) stretching modes. The vibrations between 950 and 1650 cm\(^{-1}\) can be attributed to B–H bending, and the peaks near 490 cm\(^{-1}\) likely correspond to an Al–B stretching band, as observed for \([\text{Al(BH}_4\text{)}_4]^-\) anion and for \(\text{Al(BH}_4\text{)}_3\text{NH}^-\).\(^{22,61,62}\) The N–H stretching region is represented by two intense peaks at 3240 and 3299 cm\(^{-1}\) that are slightly shifted to lower frequencies with respect to the symmetric (3250 cm\(^{-1}\)) and antisymmetric (3316 cm\(^{-1}\)) stretches in \(\text{NH}_3\text{BH}_3\).\(^{63}\) Literature reports the B–N vibrations around 800 cm\(^{-1}\), and we can surmise that the vibration at 858 cm\(^{-1}\) belongs to the B–N stretch in the coordinated \(\text{NH}_3\text{BH}_3\).\(^{63}\)

**Thermal Analysis: Two Decomposition Steps.** Several thermal effects are observed when the samples are heated from 25 to 200 °C (Figure 5a). The first endothermic (∼39 kJ/mol) peak near 46–52 °C (DSC) corresponds to the melting/decomposition of β-\(\text{Al(BH}_4\text{)}_2\cdot\text{NH}_3\text{BH}_3\). The next endothermic (∼65 kJ/mol) peak near 93 °C is assigned to the second decomposition step. TGA also displays two decomposition steps: the first starts at ∼60 °C and finishes at ∼80 °C, and the second is centered around 90 °C. The bottom part of Figure 5b shows that the higher heating rate increases the decomposition temperature from ∼60 °C for 1 °C/min to ∼77 °C for 5 °C/min. This behavior is similar to that of ammonia borane, which showed different decomposition reaction pathways depending on the heating rate.\(^{36,37}\)

We performed additional experiments aiming to separate the two decomposition steps, holding samples at fixed temperatures of 70 and 80 °C. Remarkably, the mass loss asymptotically reached very different values of 5 and 25 wt %, respectively (see...
Figure 5. Thermal analysis of the Al(BH₄)₃·NH₃BH₃ complex: (a) overlap of the TGA and DSC data collected at a rate of 1 °C/min and (b) weight loss as a function of time, at constant temperatures of 70 and 80 °C (top graph), and as a function of heating rate (bottom). (c) MS curves of evolving gases measured in the temperature range of 30–70 °C. The signals of ammonia, diborane, and borazane are close to zero level, which confirms the high purity of hydrogen release at 70 °C.

Figure 6. Volumetric analysis of Al(BH₄)₃·NH₃BH₃ decomposition at 70 °C with 0.54 mmol of the complex and at 100 °C with 0.58 mmol of the complex, at a heating rate of 1 °C/min.

The MS determination of the released gases was made in the same manner as TGA: the first decomposition step is characterized isothermally at 70 °C and the complete decomposition at temperatures above 100 °C. Remarkably, desorption at 70 °C showed exclusively the release of hydrogen, while the possible impurities of ammonia, diborane, and borazane were not detected (see Figure 5c). Further heating provokes release of diborane, which was detected around the start of the second decomposition step at 85 °C (see Figure S4 of the Supporting Information). Variable-temperature in situ Raman spectroscopy also confirmed decomposition of the complex around 75 °C (see Figure S5 of the Supporting Information). Unfortunately, the detailed characterization of the decomposition products of the first and second steps was not possible from Raman spectra. Visually, the residue of the fully decomposed (at 150 °C) samples resembles foamed polymer-like products.

**Volumetric Study of the Decomposition and a Reversibility Test.** Taking into account the information from TGA and DSC analysis, we performed two volumetric measurements at different temperatures: 70 °C, which corresponds to the first decomposition step, and 100 °C, which relates to the second decomposition step.

Samples were steadily heated at a rate of 1 °C/min, as in the TGA experiment. Decomposition at 70 °C produces ~1.15 mmol of gas from 0.54 mmol of the starting complex (Figure 6), i.e., 2.15 mol of gas per formula unit (f.u.). To verify this result, two additional volumetric experiments were conducted for the first step of the decomposition in He and H₂ backpressure at 70 °C, yielding 1.93 and 2.10 mol of gas per f.u. The second decomposition step at 100 °C shows the release of ~2.81 mmol of gas per f.u. Using the TGA data, we infer that the first decomposition step gives ~2 mol of hydrogen per Al(BH₄)₃·NH₃BH₃ unit (~5 wt % mass loss) and the second step gives almost 1 mol of diborane (close to ~25 wt % mass loss).

Our attempts to rehydrogenate, at 150 bar, the samples decomposed at 70 and 100 °C were not successful: the H₂ pressure returns exactly to the same value after the very slow cooling (see Figure S6 of the Supporting Information).

**NMR Spectroscopy Study of Al(BH₄)₃·NH₃BH₃ and Its Decomposition.** ¹H, ¹¹B, and ²⁷Al NMR spectra were recorded on Al(BH₄)₃ prior to being used in the synthesis of
Al(BH$_4$)$_3$·NH$_3$BH$_3$ and were found to be in good agreement with the literature. The interpretation of the $^1$H NMR spectra being difficult because of the presence of very broad signals around 0.5 ppm, we focused our attention on the interpretation of $^{11}$B and $^{27}$Al NMR spectra. The main $^{11}$B peak for Al(BH$_4$)$_3$ is found at $-36.3$ ppm with a negligible amount of diborane, because of the slow Al(BH$_4$)$_3$ degradation, present at 17.8 ppm (not even visible in Figure 7b). The main $^{27}$Al peak for Al(BH$_4$)$_3$ is at $99.7$ ppm, and an unknown impurity observed at 78.2 ppm (Figure 7a,b). Broad signals in the spectra originate from the solid Al-containing material in the probe, and from the $^{11}$B in the borosilicate NMR tubes, as proven by blank measurements, and can be removed by using a backward linear prediction during data processing.

Samples of Al(BH$_4$)$_3$·NH$_3$BH$_3$ stored in a glovebox at 25−30 °C over 2 weeks turned into a viscous mass, prompting us to study by NMR spectroscopy the decomposition products obtained at different temperatures. To observe the changes in Al(BH$_4$)$_3$·NH$_3$BH$_3$, we performed experiments on (1) a freshly dissolved sample in toluene-$d_8$, (2) the same sample in solution kept at room temperature for 2 and 18 h, and (3) samples heated to 70 and 100 °C, as in Volumetric Study, and then dissolved in toluene-$d_8$. Complete data are shown in Figures S8−S18 of the Supporting Information.

Al(BH$_4$)$_3$·NH$_3$BH$_3$ does not decompose into Al(BH$_4$)$_3$, as no signal at $99.7$ ppm in the $^{27}$Al NMR spectrum appears; instead, we observe a signal at 60.3 ppm that is not present after 18 h. In the $^{11}$B NMR spectrum (Figure 10b), we observe a sextuplet, consisting of two overlapped quintets at $-33.8$ and $-34.4$ ppm, and a quadruplet at $-21.9$ ppm (Figure 8b and Figures S9−S12 of the Supporting Information). The presence of a small amount of diborane B$_2$H$_6$ was observed as a triplet of triplets at 17.5 ppm in the $^{11}$B NMR spectrum. It is likely the result of partial decomposition of Al(BH$_4$)$_3$·NH$_3$BH$_3$ into B$_2$H$_6$, as for instance via a reaction

$$\text{Al(BH}_4\text{)$_3$·NH}_3\text{BH}_3 \rightarrow \text{[Al(BH}_4\text{)$_2$·(NH}_2\text{)]}_n + H_2 + B_2H_6}$$

There is no diborane forming up to 70 °C in the absence of the solvent (see the MS data in Figure 5). However, the intensity of the diborane peak increases with time in the toluene solution.

In contrast to the broad signal of the starting compound at 60.3 ppm that disappears over time, the intensity of a nonuplet
at 63.0 ppm increases in the $^{27}$Al NMR spectrum (Figures 8a and 9a). In the $^{11}$B NMR spectrum, a quintet at ~34.4 ppm, corresponding to BH$_4^-$ anion, increasingly dominates the spectrum over the disappearing signal at ~33.8 ppm present at 2 and 18 h (Figures 8b and 9b).

In the sample that decomposed at ~70 °C, the same main NMR signals, as in the 18 h-aged sample spectrum, were observed at 63 and ~34.5 ppm in the $^{27}$Al and $^{11}$B NMR spectra, respectively (compare Figures 9 and 10). The intensities of the several other minor signals at 82.0, 77.6, and 74.4 ppm changed in the $^{27}$Al spectrum. After 100 °C, we observe (Figure S18 of the Supporting Information) only a single $^{27}$Al NMR signal at 81.9 ppm, which probably has the same nature as that at 82.0 ppm after heating to 70 °C (Figure 10a).

$^{11}$B NMR signals at ~35.0 ppm are present in all the samples as well as an unknown signal in the $^{27}$Al spectrum and are suspected to belong to AlB$_x$H$_y$ products, as well as the $^{11}$B signals at ~36.0 ppm with $^{27}$Al at 81.9 and 82.0 ppm. They can be the result of reaction of B$_3$H$_6$ with starting compound or/and forming products previously described for Al(BH$_4$)$_3$ with B$_2$H$_6$, giving the AlB$_4$H$_11$ at 100 °C. The assignment of the remaining weak $^{11}$B signals is not certain, but they likely belong to polyhydroboranes. The presence of compounds such as DADB [BH$_4$(NH$_3$)$_3$]BH$_4$ is excluded because no characteristic BH$_4^-$ signal at approximately ~15 ppm on the $^{11}$B spectrum was detected in our experiment.

Notably, the fresh Al(BH$_4$)$_3$·NH$_3$BH$_3$ sample kept in a toluene-$d_8$ solution at room temperature, the sample aged in the inert atmosphere at ambient temperature and then dissolved in toluene-$d_8$ (Figure S19 of the Supporting Information), and the sample heated to 70 °C and then dissolved in toluene-$d_8$ all give the same spectral features. No insoluble products were formed upon their dissolution in toluene. Therefore, it is likely the same decomposition pathway is followed in toluene solutions and in the absence of any solvent. This means we can interpret by NMR the decomposition intermediate obtained in TGA/DSC and volumetric experiments, responsible for the release of 2 mol of H$_2$. Its fingerprint is the nonuplet at 63.0 ppm in the $^{27}$Al NMR spectrum, with an intensity distribution of 14:22:40:64:70:64:40:22:14. With proton decoupling, this nonuplet at 63.0 ppm becomes a singlet (Figures S12a,b and S15a,b), implying the splitting of this peak into nine lines is indeed caused by protons coupled to aluminum. The experimental signal exhibits nine maxima or shoulders, but as
one can see in Figure 11a, it is not properly described by a first-order nonuplet (relative intensity ratios of 1:8:28:56:70:56:28:8:1; four adjustable parameters being chemical shift, line width, overall intensity, and one scalar coupling constant). In contrast, considering a doublet of heptuplets as a model yields excellent agreement (Figure 11b; relative intensity ratios of {1:6:15:20:15:6:1}; five adjustable parameters, including the overall intensity). The relevant best-fit parameters are as follows: \( \delta = 62.954 \) ppm, \( \Delta \nu_{1/2} = 40.0 \) Hz (full line width at half-height corrected for \( \nu \)), and scalar coupling constants \( J_{\text{doublet}} = 89.4 \) Hz, \( J_{\text{heptuplet}} = 46.4 \) Hz. Our observed \( J \) value of 46.4 Hz is similar to that reported for \( J_{\text{AlH}} \) of 44 Hz in Al(BH₄)₃. ⁶⁷

**Decomposition Intermediate.** The NMR study shows that the first step of the decomposition of Al(BH₄)₃•NH₄BH₄ yields the product in which an Al ion is bound to three borohydride anions with edges and further bound to one hydrogen, most likely a part of an “HN-HB” molecule or its oligomers, as shown here:

![Decomposition Intermediate](image)

This evidence ties in very well with the results of our volumetric/TGA data suggesting the loss of two H₂ molecules. The \( 6H + 1H \) coordination of Al in the decomposition intermediate of Al(BH₄)₃•NH₄BH₄ is the first evidenced by the deconvolution analysis of the \( ^{27} \)Al NMR spectrum. The molecular structure of the other aluminum borohydride complexes had been previously assigned on the basis of the supposed reaction equilibria in solutions and the known solid-state structures.⁶⁰,⁶⁸ In all cases, the BH₄ anions are coordinated via the BH₂ edges. Broad singlets at 49.5 ppm in the spectra of [Ph₃MeP][Al(BH₄)₄] and [(Ph₃P)₂N][Al(BH₄)₃] in CD₂Cl₂ correspond to 8 equiv of H around Al,⁶⁹ and that at 99.7 ppm in the spectrum of Al(BH₄)₃ corresponds to 6 equiv of H around Al; both are significantly different from the 63.0 ppm shift we observed. The complex with the closest chemical shift is \([\text{AlH(BH}_4)_2]_n\) with a signal at 64.7 ppm: it contains 4H from the BH₄ groups and 2H bridging Al atoms.⁶⁴

### CONCLUSIONS

The thermal decomposition of the new complex, Al(BH₄)₃•NH₄BH₄, showed several striking features as compared with those of the previously investigated systems involving ammonia borane. We found that the decomposition of the complex in toluene solutions and upon heating the solid gives the same intermediate, releasing 2 equiv of hydrogen at 70 °C. It occurs at a temperature considerably lower than that for the pure NH₄BH₄ desorbing the first equivalent at 120 °C and the second at 150 °C.⁶⁹ To the best of our knowledge, this is the first metal borohydride—ammonia borane complex, resulting in hydrogen release. The other systems produce significant amounts of ammonia, diborane, and borazine on the first decomposition step.⁴⁶—⁴⁹ Also, we do not observe polyamino-boranes (PAB) and polyborazylene, which form during liquid-state pyrolysis of NH₄BH₄ in ionic liquids and in the presence of strong Lewis and Brønsted acids. They would result in \( ^{11} \)B signals in the range of \(-10\) to \(-13 \) ppm for BH₂⁺, near \(-5 \) ppm for N—BH₄—N, and near \(-22 \) ppm from BH₄ polymer terminating groups for PAB and 26 ppm for polyborazylene.⁷⁰,⁷¹

The favorable decomposition pathway and the decomposition temperature make this system an attractive model for efficient elimination of hydrogen from ammonia borane. Taking into account all our data, we conclude that the decomposition of the staring complex into the Al-based intermediate can be assigned to Al(BH₄)₃ as a unique mild Lewis acid that coordinates both the starting and the dehydrogenated BH₄ groups (n = 1 or 3). This urges us to use other Al-based Lewis acids, less challenging with respect to stability and safety than aluminum borohydride.

This system is also encouraging in terms of a possible direct rehydrogenation of ammonia borane, which is currently regenerated successfully only via multistep chemical cycles.⁷² The striking property of the title system is the endothermic dehydrogenation on the first decomposition step (39 kJ/mol, including melting), compared to the exothermic one for ammonia borane (\(-22 \) kJ/mol on the first decomposition step, including melting).⁶⁶ Despite our first attempts to directly rehydrogenate the intermediate that were not successful, a catalyzed reaction may be possible.
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